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Preparation of metallocene catalysts for polymerization of olefins.

This invention uses a new method of producing ionic metallocene compounds. These compounds are useful as catalysts for polymerization of olefins, primarily propylene. This method uses an ionizing agent which ionizes the neutral metallocene compound. The ionizing ionic compound does not contain an active proton and contains a carbonium, oxonium or sulfonium cation. The anion of the ionizing ionic compound is not coordinated or is only loosely coordinated to the metallocene cation and is chemically unreactive with the metallocene cation. One such compound is triphenylcarbenium tetrakis(pentafluorophenyl)boronate.

The process of making catalysts with this invention produces catalysts having high activity and does not produce by-products which can inhibit catalyst activity. This new synthesis is a clean reaction which does not produce a Lewis base. The process generates active catalysts by removing a methyl anion from a group IV metallocene derivative.

EP 0 426 637 A2

PREPARATION OF METALLOCENE CATALYSTS FOR POLYMERIZATION OF OLEFINS

SPECIFICATION

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BACKGROUND OF THE INVENTION

10 FIELD OF THE INVENTION:

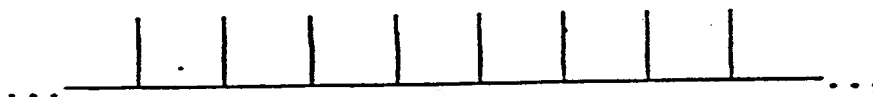
This invention relates, in general, to a process for preparing catalysts and, specifically, to a process for preparing catalysts for polymerization of olefins.

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DESCRIPTION OF RELATED ART:

Olefins, especially propylene, may be polymerized to form polyolefins in various forms: isotactic, syndiotactic and atactic. Isotactic polypropylene contains principally repeating units with identical configurations and only a few erratic, brief inversions in the chain. Isotactic polypropylene may be structurally represented as

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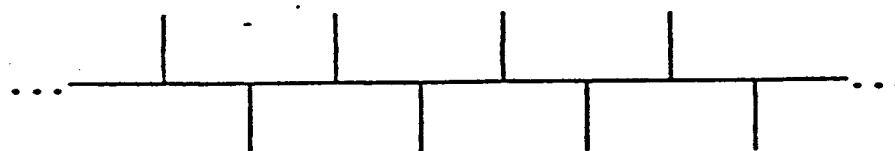


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Isotactic polypropylene is capable of being a highly crystalline polymer with a high melting point and other desirable physical properties that are considerably different from the polymer in an amorphous (noncrystalline) state.

A syndiotactic polymer contains principally units of exactly alternating stereoisomers and is represented by the structure:

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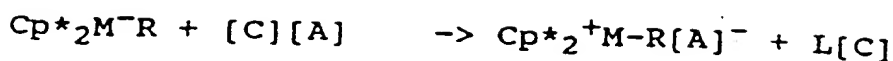
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A polymer chain showing no regular order of repeating unit configurations is an atactic polymer. In commercial applications, a certain percentage of atactic polymer is typically produced with the isotactic form.

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Polymerization of olefins is primarily with Zeigler-Natta catalysts. One family of Zeigler-Natta catalysts is Group IV metallocene compounds with methylaluminoxane as a cocatalyst. It has been demonstrated that Zeigler-Natta catalysts for olefin polymerization can be formed by combining a group IV metallocene with an ionic compound.

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L

Cp* - pentamethylcyclopentadienyl

M - Group IV metal

R - alkyl

L - ligand

[C] - cation

[A] - anion

The resulting compound is a metallocene cation which acts as a catalyst. The cation [C] of the ionic compound reacts with the metallocene to generate an ion pair. The anion, [A], is not coordinated or is only loosely coordinated with the cationic metallocene.

The following methods have been used to produce the above reaction:

One-Electron Oxidation - This method is illustrated in "Ethylene Polymerization by a Cationic Dicyclopentadienylzirconium(IV) Alkyl Complex", R.F. Jordan, C.S. Bajgur, R. Willett, B. Scott, J. Am. Chem. Soc., p. 7410-7411, Vol. 108 (1986). These early examples used a Lewis base to make the metal cation less electrophilic and [BPh₄]⁻ was the anion where Ph is C₆H₅. The reaction occurred in a coordinating solvent. These catalysts were usually of low activity.

Protonation - This method is illustrated by "Synthesis and Insertion Reactions of Cationic Alkylbis(cyclopentadienyl)titanium Complexes", M. Bochmann, L.M. Wilson, J. Chem. Soc. Commun., p. 1610-1611, (1986); "Cationic Alkylbis(cyclopentadienyl)titanium Complexes", M. Bochmann, L. Wilson, Organometallics, p. 2556-2563, Vol. 6, (1987); Insertion Reactions of Nitriles in Cationic Alkylbis(cyclopentadienyl)titanium Complexes, M. Bochmann, L. Wilson, Organometallics, p. 1147-1154, Vol. 7 (1987).

European Patent Application 0-277-003 relates to work by Turner on a catalyst prepared by a protonation method. A bis(cyclopentadienyl) metal compound is combined with a compound having a cation capable of donating a proton and an anion having a plurality of boron atoms. For example, the following reaction illustrates the invention:

bis(cyclopentadienyl)hafnium dimethyl + N,N-dimethylanilinium bis(7,8-dicarbaundecaborato) cobaltate(III) → [Cp₂HfMe]⁺[B] + CH₄ + N,N-dimethylaniline
where [B] is 7,8-dicarbaundecaborane.

European Patent Application 0-277-004 also relates to work by Turner on a catalyst prepared by a protonation method. A bis(cyclopentadienyl) metal compound is combined with an ionic compound having a cation which will irreversibly react with a ligand on the metal compound and an anion having a plurality of lipophilic radicals around a metal or metalloid ion. For example, the following reaction illustrates the invention:

tri(n-butyl)ammonium tetra(pentafluorophenyl)boron + bis(cyclopentadienyl)zirconium dimethyl → [Cp₂ZrMe]⁺[BPh₄]⁻ + CH₄ + tri(n-butyl)N

A by-product of the protonation reaction is a Lewis base (amine) some of which can coordinate to the cations and thus inhibit catalyst activity. Starting materials must be chosen carefully to avoid generating particular amines which are catalyst poisons. In addition, the catalyst and the polymer produced with this catalyst contains undesirable and toxic residual amines.

Ligand abstraction - The ligand abstraction method is illustrated in "Multiple Metal-Carbon Bonds", R. Schrock, P. R. Sharp, J. Am. Chem. Soc., p. 2389-2399, Vol. 100, No. 8 (April, 2, 1978).

In most known processes, methylaluminoxane (MAO) is added with the metallocene compound to act as a cocatalyst. The function of MAO is to initiate the alkylation and promote ionization of the metallocene compound. The cocatalyst is a scavenging agent which reduces the poisons which decrease catalyst activity. Present known processes require a large excess of MAO to be added. MAO has the disadvantage

of being relatively expensive. This results in high costs for the catalyst system.

SUMMARY OF THE INVENTION

Accordingly, it is an object of this invention to provide a process for making an improved catalyst for polymerization of olefins.

And, it is an object of this invention to provide a process for making a catalyst with relatively high activity.

Also, it is an object of this invention to synthesize metallocene cations with no Lewis base as a side product.

Further, it is an object of this invention to eliminate the necessity to chose starting materials to control the by-products which may be produced as catalyst poisons.

Additionally, it is an object of this invention to eliminate methylaluminoxane (MAO) as a cocatalyst in polymerization of polypropylene.

Moreover, it is an object of this invention to produce polymers which are free of aluminum oxide.

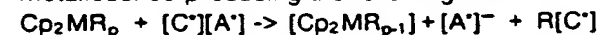
As well, it is an object of this invention to produce a polymer which is free of undesirable and toxic amines.

These and other objects are accomplished by mixing an ionizing agent, such as triphenylcarbenium tetrakis(pentafluorophenyl)boronate, with derivatives of metallocenes and adding the mixture to an olefin.

DESCRIPTION OF THE INVENTION

The invention is for a process of producing a catalyst for polymerization of olefins by ionizing a metallocene with an ionizing agent which does not contain an active proton and which has an anion which is not coordinated or is only loosely coordinated to the cation of the metallocene. The anion is also chemically unreactive with the cation.

In the new synthesis procedure the ionizing ionic compound is mixed with neutral derivatives of metallocenes producing the following reaction:



where Cp is a cyclopentadienyl or a substituted cyclopentadienyl group, each Cp being the same or different, M is a Group III, IV, V or VI metal, R is a hydride, a halogen, an amide or a hydrocarbyl radical, each R being the same or different, except that if R is a hydride only one R is a hydride, p is from 1 to 4, C⁺ is a carbonium, oxonium or sulfonium cation and A⁻ is an anion which is not coordinated or is only loosely coordinated to the cation of the metallocene and is chemically unreactive with [Cp₂MR_{p-1}].

Each reactant is placed in a solvent which is not coordinated or is only loosely coordinated with the metallocene cation. Examples of such solvents are toluene and methylene chloride. The preferred solvent is toluene. The two reactants are dissolved separately in the same solvent and are mixed together at room temperature at a mole ratio ranging from 10 moles of metallocene : 1 mole of ionizing compound to 1 mole of metallocene : 10 moles of ionizing compound. A preferred mole ratio is from 2 moles of metallocene : 1 mole of ionizing compound to 1 mole of metallocene : 2 moles of ionizing compound. The most preferred mole ratio is 1 mole of metallocene : 1 mole of ionizing compound. After mixing, the mixture is added to an olefin under conditions to effect polymerization. The preferred olefins are ethylene and propylene, the most preferred being propylene.

An ionic compound containing a carbonium, oxonium or sulfonium ion, such as triphenylcarbenium tetrakis(pentafluorophenyl)boronate, is mixed with a neutral derivative of a metallocene. Triphenylcarbenium tetrakis(pentafluorophenyl)boronate acts as an ionizing agent which ionizes the metallocene. A cationic metallocene catalyst is formed.

Triphenylcarbenium tetrakis(pentafluorophenyl)boronate [Ph₃C][BPh₄⁻] is produced by the following reaction:

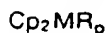


where Ph is phenyl and Ph⁻ is pentafluorophenyl. Triphenylcarbenium is a cation. Tetrakis(pentafluorophenyl) boronate is an anion.

Triphenylcarbenium tetrakis(pentafluorophenyl)boronate was produced with the following laboratory method. A bright yellow solution of 27.1 mmoles of Ph₃CCl in 150 cc of methylene chloride was added

dropwise at 25°C to 25 gm of $\text{LiB}(\text{C}_6\text{F}_5)_4$ slurried in 350 cc of methylene chloride. The orange slurry was stirred for 30 minutes and then filtered. The solids containing $[\text{Ph}_3\text{C}][\text{BPh}_4]$ and LiCl were washed with methylene chloride. The combined wash and filtrate was concentrated to 75 cc and then cannulated into 400 cc of pentane with rapid stirring. The solids were washed several times with pentane and small amounts of toluene until a bright yellow powder of $[\text{Ph}_3\text{C}][\text{BPh}_4]$ was obtained. The yield was 20 grams (75%).

The neutral derivative of a metallocene is of the general formula:



wherein Cp is a cyclopentadienyl or a substituted cyclopentadienyl group, each Cp being the same or different, M is a Group III, IV, V or VI metal, preferably a Group IV metal, such as titanium, hafnium or zirconium, most preferably zirconium for higher catalyst activity and hafnium for higher molecular weight, R is a hydride, a halogen, an amide or a hydrocarbyl radical such as an alkyl, aryl, alkenyl, alkylaryl or arylalkyl radical having from 1 to 20 carbon atoms, each R being the same or different, except that if R is a hydride only one R is a hydride and p is from 1 to 4. The preferred neutral derivatives of metallocene are ethylene bis(tetrahydroindenyl)zirconium dimethyl, ethylenebis(indenyl)zirconium dimethyl and isopropylidene(cyclopentadienyl-1-fluorenyl)zirconium dimethyl. The most preferred neutral derivative of metallocene is ethylene bis(indenyl)zirconium dimethyl.

Polymerization of the olefin is accomplished by any of the known means for polymerization of olefins with metallocene catalysts, for example polymerization in bulk, slurry or gas phase. For polypropylene, polymerization temperatures range from -80°C to 150°C, preferably 25°C to 90°C and most preferably from 50°C to 80°C.

The invention having been generally described, the following examples are given as particular embodiments of the invention and to demonstrate the practice and advantages thereof. It is understood that the examples are given by way of illustration and are not intended to limit the specification or the claims to follow in any manner.

EXAMPLE I

55 mg of triphenylcarbenium tetrakis(pentafluorophenyl) boronate was dissolved in 5 cc of toluene. 40 mg of $\text{Et}(\text{IndH}_4)_2\text{ZrMe}_2$ was dissolved in 5 cc of toluene. The two solutions were mixed together for 5 minutes at room temperature, giving a clear yellow solution.

The mixture was added by syringe to a 2 liter Zipperclave reactor. 1.0 liter of propylene was added to the reactor. Reactor temperature was set to 70°C. The contents of the reactor were agitated. The temperature remained at 70°C during the sixty minute polymerization period after which propylene was vented from the reactor. The contents of the reactor were washed with acetone and dried in a vacuum oven.

The polymer was analyzed for melting point. The melting point was derived from differential scanning calorimetry (DSC). The results are shown in Table I.

EXAMPLE II

The procedure of Example I was repeated using 40 mg of triphenylcarbenium tetrakis-(pentafluorophenyl)boronate and 20 mg of $\text{Et}(\text{IndH}_4)_2\text{ZrMe}_2$. The results are shown in Table I.

EXAMPLE III

The procedure of Example I was repeated using 30 mg of triphenylcarbenium tetrakis-(pentafluorophenyl)boronate and 15 mg of $\text{Et}(\text{IndH}_4)_2\text{ZrMe}_2$. The reactor temperature was set at 80°C and the temperature remained at 80°C. The results are shown in Table I.

EXAMPLE IV

The procedure of Example I was repeated using 60 mg of triphenylcarbenium tetrakis-(pentafluorophenyl)boronate and 60 mg of $\text{Et(IndH}_4\text{)ZrMe}_2$. Reactor temperature was set at 50°C and the temperature remained at 100°C. Run time was 10 minutes. The results are shown in Table I.

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EXAMPLE V

10 The procedure of Example I was repeated using 55 mg of triphenylcarbenium tetrakis-(pentafluorophenyl)boronate and 50 mg of $\text{Et(IndH}_4\text{)ZrMe}_2$. Reactor temperature was set at 50°C and increased to 168°C. Run time was 10 minutes. The results are shown in Table I.

EXAMPLE VI

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The procedure of Example I was repeated using 100 mg of triphenylcarbenium tetrakis-(pentafluorophenyl)boronate and 60 mg of $\text{Et(Ind)}_2\text{ZrMe}_2$. Reactor temperature was set at 50°C and the temperature remained at 50°C. The results are shown in Table I.

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EXAMPLE VII

25 The procedure of Example I was repeated using 100 mg of triphenylcarbenium tetrakis-(pentafluorophenyl)boronate and 60 mg of $\text{Et(Ind)}_2\text{ZrMe}_2$. The temperature was set at 50°C and remained at 50°C. The results are shown in Table I.

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EXAMPLE VIII

35 The procedure of Example I was repeated using 120 mg of triphenylcarbenium tetrakis-(pentafluorophenyl)boronate and 80 mg of $\text{iPr(Cp-1-Flu)ZrMe}_2$. Reactor temperature was set at 70°C and the temperature increased above 100°C. The results are shown in Table I.

EXAMPLE IX

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The procedure of Example I was repeated using 100 mg of triphenylcarbenium tetrakis-(pentafluorophenyl)boronate and 60 mg of $\text{iPr(Cp-1-Flu)ZrMe}_2$. Reactor temperature was set at 70°C and the temperature increased to 78°C. The results are shown in Table I.

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EXAMPLE X

50 The procedure of Example I was repeated using 60 mg of triphenylcarbenium tetrakis-(pentafluorophenyl)boronate and 40 mg of $\text{iPr(Cp-1-Flu)ZrMe}_2$. Reactor temperature was set at 70°C. The results are shown in Table I.

The following results are from the experimental runs described above using the method of the present invention.

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TABLE I

RUN #	CATALYST, + mg	IONIZING AGENT, + + mg	TIME, min.
	Et(IndH ₄) ₂ ZrMe ₂	[Ph ₃ C][BPh ₄]	
1	40	55	60
2	20	40	60
3	15	30	80
4	50	60	10
5	50	55	10
	Et(Ind) ₂ ZrMe ₂	[Ph ₃ C][BPh ₄]	
6	60	100	60
7	60	100	30
	iPr(Cp-1-Flu)ZrMe ₂	[Ph ₃ C][BPh ₄]	
8	80	120	5
9	60	100	60
10	40	60	60

+ Et(IndH₄)₂ZrMe₂ = Ethylenebis(tetrahydroindenyl)zirconium dimethyl
 Et(Ind)₂ZrMe₂ = Ethylenebis(indenyl)zirconium dimethyl
 iPr(Cp-1-Flu)ZrMe₂ = isopropylidene (cyclopentadienyl-1-fluorenyl)zirconium dimethyl
 + + [Ph₃C][BPh₄] = triphenylcarbenium tetrakis(pentafluorophenyl)boronate.

RUN #	TEMP, °C	YIELD, gm	Melting Temp °C
1	70	9	138
2	50	55	138
3	80	45	131
4	50*	74	134
5	50*	135	-
6	50	19	137
7	50	11	134
8	70*	224	115
9	70**	51	-
10	70***	186	119

*Runaway reaction; peak reaction temperature > 100°C

**Exotherm; peak reaction temperature 78°C

***Exotherm

The process described by this invention synthesizes cations which are used as catalysts in olefin polymerization. The process of making catalysts with this invention produces catalysts having high activity and does not produce by-products which can inhibit catalyst activity. This new synthesis is a clean reaction which does not produce a Lewis base. The process generates active catalysts by removing a methyl anion from a group IV metallocene derivative.

Obviously, numerous modifications and variations of the present invention are possible in light of the

above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

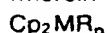
5 Claims

1. A process for making a catalyst comprising:

a) mixing an ionizing ionic compound with a neutral derivative of a metallocene; and

10 b) allowing contact between the ionizing ionic compound and the neutral derivative of a metallocene such that the metallocene is ionized by the ionizing ionic compound and an ion pair is formed in which the metallocene cation acts as a catalyst;

wherein the neutral derivative of a metallocene is of the general formula:



15 wherein Cp is a cyclopentadienyl or a substituted cyclopentadienyl group, each Cp being the same or different, M is a Group III, IV, V or VI metal, R is a hydride, a halogen, an amide or a hydrocarbyl radical, each R being the same or different, except only one R is a hydride and p is from 1 to 4;

wherein the ionizing ionic compound does not contain an active proton and contains a carbonium, oxonium or sulfonium cation; and

20 wherein the anion of the ionizing ionic compound is not coordinated or is only loosely coordinated to the metallocene cation and is chemically unreactive with the metallocene cation.

2. A process as recited in Claim 1 wherein, before mixing, the ionizing ionic compound is dissolved in a solvent which is not coordinated or is only loosely coordinated with the metallocene cation.

3. A process as recited in Claim 2 wherein, before mixing the neutral derivative of a metallocene is separately dissolved in the same solvent.

25 4. A process as recited in Claim 3 wherein the mole ratio of the neutral derivative of a metallocene to the ionic compound ranges from 10 moles of metallocene : 1 mole of ionizing compound to 1 mole of metallocene : 10 moles of ionizing compound.

5. A process as recited in Claim 4 wherein the mole ratio of the neutral derivative of a metallocene to the ionic compound ranges from 2 moles of metallocene : 1 mole of ionizing compound to 1 mole of 30 metallocene : 2 moles of ionizing compound.

6. A process as recited in Claim 5 wherein the mole ratio of the neutral derivative of a metallocene to the ionic compound ranges is 1 mole of metallocene : 1 mole of ionizing compound.

7. A process as recited in Claim 4 wherein the metal is a Group IV metal chosen from the group consisting of titanium, zirconium and hafnium.

35 8. A process as recited in Claim 7 wherein the metal is hafnium.

9. A process as recited in Claim 7 wherein the metal is zirconium.

10. A process as recited in Claim 9 wherein R is a hydrocarbyl radical chosen from the group consisting of an alkyl radical, an aryl radical, an alkenyl radical, an alkylaryl radical and an arylalkyl radical having from 1 to 20 carbon atoms.

40 11. A process as recited in Claim 10 wherein the neutral derivative of a metallocene is chosen from the group consisting of ethylene bis(tetrahydroindenyl)zirconium dimethyl, ethylene bis(indenyl)zirconium dimethyl and isopropylidene (cyclopentadienyl-1-fluorenyl)zirconium dimethyl.

12. A process as recited in Claim 11 wherein the neutral derivative of a metallocene is ethylenebis(indenyl) zirconium dimethyl.

45 13. A process as recited in Claim 12 wherein the ionic compound is triphenylcarbenium tetrakis-(pentafluorophenyl) boronate.

14. A process as recited in Claim 13 wherein the solvent is toluene.

15. A process for polymerization of an olefin comprising:

a) mixing an ionizing ionic compound with a neutral derivative of a metallocene;

50 b) allowing contact between the ionizing ionic compound and the neutral derivative of a metallocene such that the metallocene is ionized by the ionizing ionic compound and an ion pair is formed in which the metallocene cation acts as a catalyst; and

c) contacting the catalyst with the olefin under conditions to effect polymerization;

wherein the neutral derivative of a metallocene is of the general formula:



55 wherein Cp is a cyclopentadienyl or a substituted cyclopentadienyl group, each Cp being the same or different, M is a Group III, IV, V or VI metal, R is a hydride, a halogen, an amide or a hydrocarbyl radical, each R being the same or different, except only one R is a hydride and p is from 1 to 4;

wherein the ionizing ionic compound does not contain an active proton and contains a carbonium, oxonium or sulfonium cation; and

wherein the anion of the ionizing ionic compound is not coordinated or is only loosely coordinated to the metallocene cation and is chemically unreactive with the metallocene cation.

- 5 16. A process as recited in Claim 15 wherein, before mixing, the ionic compound is dissolved in a solvent which is not coordinated or is only loosely coordinated with the metallocene cation.
17. A process as recited in Claim 16 wherein, before mixing, the neutral derivative of a metallocene is dissolved in the same solvent.
18. A process as recited in Claim 17 wherein the mole ratio of the neutral derivative of a metallocene to the
10 ionic compound ranges from 10 moles of metallocene : 1 mole of ionizing compound to 1 mole of metallocene : 10 moles of ionizing compound.
19. A process as recited in Claim 18 wherein the mole ratio of the neutral derivative of a metallocene to the ionic compound ranges from 2 moles of metallocene : 1 mole of ionizing compound to 1 mole of metallocene : 2 moles of ionizing compound.
- 15 20. A process as recited in Claim 19 wherein the mole ratio of the neutral derivative of a metallocene to the ionic compound ranges is 1 mole of metallocene : 1 mole of ionizing compound.
21. A process as recited in Claim 18 wherein the metal is a Group IV metal chosen from the group consisting of titanium, zirconium and hafnium.
22. A process as recited in Claim 21 wherein the metal is hafnium.
- 20 23. A process as recited in Claim 21 wherein the metal is zirconium.
24. A process as recited in Claim 23 wherein R is a hydrocarbyl chosen from the group consisting of an alkyl radical, an aryl radical, an alkenyl radical, an alkylaryl radical and an arylalkyl radical having from 1 to 20 carbon atoms.
25. A process as recited in Claim 24 wherein the neutral derivative of a metallocene is chosen from the
25 group consisting of ethylene bis(tetrahydroindenyl)zirconium dimethyl, ethylene bis(indenyl)zirconium dimethyl and isopropylidene (cyclopentadienyl-1-fluorenyl)zirconium dimethyl.
26. A process as recited in Claim 25 wherein the neutral derivative of a metallocene is ethylene bis-(indenyl)zirconium dimethyl.
27. A process as recited in Claim 26 wherein the ionic compound is triphenylcarbenium tetrakis-
30 (pentafluorophenyl) boronate.
28. A process as recited in Claim 27 wherein the solvent is toluene.
29. A process as recited in Claim 28 beginning at a reaction temperature which ranges from -80°C to 150°C.
30. A process as recited in Claim 29 beginning at a reaction temperature which ranges from 25°C to 90°C.
- 35 31. A process as recited in Claim 30 beginning at a reaction temperature which ranges from 50°C to 80°C.

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(54) Preparation of metallocene catalysts for polymerization of olefins.

(57) This invention uses a new method of producing ionic metallocene compounds. These compounds are useful as catalysts for polymerization of olefins, primarily propylene. This method uses an ionizing agent which ionizes the neutral metallocene compound. The ionizing ionic compound does not contain an active proton and contains a carbonium, oxonium or sulfonium cation. The anion of the ionizing ionic compound is not coordinated or is only loosely coordinated to the metallocene cation and is chemically unreactive with the metallocene cation. One such compound is triphenylcarbenium tetrakis-(pentafluorophenyl)boronate.

The process of making catalysts with this invention produces catalysts having high activity and does not produce by-products which can inhibit catalyst activity. This new synthesis is a clean reaction which does not produce a Lewis base. The process generates active catalysts by removing a methyl anion from a group IV metallocene derivative.

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EP 0 426 637 A3

EUROPEAN SEARCH
REPORT

EP 90 87 0174

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,A	EP-A-0 277 003 (EXXON) * Page 6, lines 42-59 * - - - -	1	C 08 F 4/76 C 08 F 4/603 C 08 F 10/00
D,A	EP-A-0 277 004 (EXXON) * Page 6, line 61 - page 7, line 7 * - - - -	1	
D,A	JOURNAL OF AMERICAN CHEMICAL SOCIETY, vol. 108, 1986, pages 7410-7411, American Chemical Society; R.F. JORDAN et al.: "Ethylene polymerization by a cationic dicyclopentadienylzirconium(IV) alkyl complex" - - - - -	1	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 08 F
Place of search		Date of completion of search	Examiner
The Hague		08 May 91	DE ROECK R.G.
CATEGORY OF CITED DOCUMENTS			
X: particularly relevant if taken alone		E: earlier patent document, but published on, or after the filing date	
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A: technological background		L: document cited for other reasons	
O: non-written disclosure		- - - - -	
P: intermediate document		Δ: member of the same patent family, corresponding document	
T: theory or principle underlying the invention			

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